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Analysis of Heavy Metals Contamination Levels in Drinking Water Collected from Different Provinces of Pakistan

[1]M. Muneeb-ur-Rehman Khattak, [1]Bakhtiar Muhammad and [2]Muhammad Zahoor

[1]Department of Chemistry, Hazara University, Mansehra, KPK, Pakistan
[2]Department of Chemistry University of Malakand Chakdarra, KPK, Pakistan

Abstract: In the present study drinking water samples were collected from selected districts of four provinces of Pakistan. About 800 drinking water samples were collected from the four provinces of Pakistan randomly and analyzed for the trace metal i.e. Ar, Pb, Cr, Cu and Zn using Atomic absorption spectrophotometer. The results of KPK province of Pakistan showed that maximum mean concentration of Ar 0.00268 mg/kg in sample collected from Mardan district whereas the highest mean contents of Pb 0.0005447mg/kg was recorded in the sample from Peshawar regions followed by Abbottabad 0.00009380mg/kg. The results of Punjab province revealed that the highest maximum mean concentration of Ar was 0.0338 mg/kg in the samples collected from district Gujranwala and the lowest maximum mean concentration of Ar was detected in the samples of Faisalabad 0.0002021 mg/kg. The maximum mean conctration of Pb was found high 0.00360 mg/kg while the lowest was recorded 0.001956 mg/kg in the samples collected from the district Faisalabad. In the samples collected from Sind province the highest maximum mean concentration of Cu 0.1888 mg/kg was observed in the samples of Karachi while the lowest was recorded 0.0000 mg/kg in the samples of Hyderabad. The Samples collected from Balochistan province showed the highest maximum mean concentration of Ar 0.0116 mg/kg in the samples of Zhob while the highest concentration of Pb was detected 0.000608 mg/kg in the samples of Jaffarabad.

Key words: Pakistan · Kpk · Punjab · Sind · Baluchistan · Ar · Pb and Zn

INTRODUCTION

Groundwater is the major source of water supply for agriculture, industrial and domestic purposes in urban as well as rural parts of the world. Among the various reasons, the most important are non-availability of potable surface water and a general belief is that groundwater is purer and safer than surface water due to the protective qualities of the soil cover. It has been estimated that approximately one third of the world's population use groundwater for drinking [1]. However, due to rapid industrialization and enormous increase in population groundwater sources are subjected to contamination with various organic and inorganic pollutants. The problems of ground water quality are more acute in areas that are densely populated and thickly industrialized and have shallow groundwater tables [2]. Also in the developing countries industrial waste water, sewage sludge and solid waste materials comprising of various inorganic and organic pollutants are currently being discharged into the environment indiscriminately. These materials enter subsurface aquifers, resulting in the pollution of irrigation and ground water [3]. The heavy metals when present in these effluents are concentrated in the biota, depending on the accumulation factors of the individual metals, thus constituting a potential source of direct intake to man [4, 5 and 6]. Most of the heavy metal ions are toxic to living organisms [7]. They are not biodegradable and are persistent [8]. The presence of these heavy metals in water can be detrimental to a variety of species including human. Therefore, the elimination of heavy metals from waters and wastewaters is important to protect public health [9].

The heavy metal levels in wastewater, drinking water and water used for agriculture must be reduced to the maximum permissible concentration. Even though most of the mortality and morbidity Associated with water-related disease in developing countries is directly due to toxic substances as arsenic, fluoride, lead, manganese, chromium, copper, iron and zinc which can lead to several

Corresponding Author: M. Muneeb-ur-Rehman Khattak, Department of Chemistry, Hazara University, Mansehra, KPK, Pakistan.

water-born diseases. The toxicity caused by heavy metals has been reported by a number of authors from various parts of the world [10, 11, 12, 13, 14, 15 and 16]. The known fatal effects of heavy metal toxicity include damaged or reduced mental and central nervous function and lower energy level. They also cause irregularity in blood composition, badly affect vital organs such as kidneys and liver. The long-term exposure of these metals result in physical, muscular and neurological degenerative processes that cause Alzheimer's disease (brain disorder), Parkinson's disease (degenerative disease of the brain), muscular dystrophy (progressive skeletal muscle weakness) and multiple sclerosis (a nervous system disease that affects brain and spinal cord) [17]. Toxicity can result from any of the heavy metals but eight of them are considered by the Agency for toxic substances and disease registry in the top 20 hazardous substances list. These metals include arsenic (Ar), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg) and platinum (Pt) [18]. Keeping in view the importance of heavy metals regarding their toxicity the present study was mainly aimed to analyze heavy metals in the drinking water samples collected from different districts of Pakistan.

MATERIALS AND METHODS

Drinking water samples of four Provinces of Pakistan were evaluated for five heavy metals *viz.* Ar, Pb, Cr, Cu and Zn contamination. Sampling was taken in random manner from different localities from all over Pakistan and transferred to PCRWR and PCSIR labs complex Peshawar for further analysis.

Samples Collection: Clean polythene screw capped bottles of 600 ml capacity were used to collect the samples from the underground water sources. Each sample bottle was washed with a brush and phosphate free detergent, three times with tap water, soaked in 10% hydrochloric acid, again washed with tap water and finally rinsed three times with de ionized water. Then these bottles were dried in sunlight and kept in the oven at 60°C for 12 hours, cooled to room temperature, recapped and labeled before collection of samples. Three samples (1, 2 and 3) were collected from each source. At the time of sampling bottles were rinsed with sample water. All necessary measures were taken during samples filling, transport and storage. Before starting the analysis all the glassware's were washed on the same procedure as the sample bottles were washed.

Heavy Metals Analysis: Heavy metals like Ar, Pb, Cr, Cu and Zn were determined with the help of Atomic Absorption spectrometry by using standard method of [11]. Atomic Absorption spectrometry (AAR) was one of the most commonly used instrumental techniques of analysis for the quantification of metals and metalloid in water and food samples. The Atomic Absorption Spectrophotometer Model (Perkins Elmer 2000) was used for the analysis of water samples.

RESULTS

The ANOVA results of arsenic level in KPK water are shown in Table 2. Arsenic was found significantly different in all districts ($P \leq 0.05$) having the value of F=15.3 while the significant difference among different districts of KPK was 0.00.

Table 3 presents the mean values for Ar of Abbottabad was significantly different from that of district Peshawar and Mardan, while no significant difference in the mean concentration of Ar was noted between Abbottabad and DI Khan. The concentration of Ar in the samples collected district Peshawar showed significant difference to that of district Abbottabad, Mardan and DI Khan. The mean values for Ar in the samples collected from district Mardan showed significant difference to the mean values of Abbottabad, Peshawar and DI Khan. No significant difference in the mean values of Ar were observed in the samples collected from DI Khan and Abbottabad, whereas significant difference in the mean concentration of Ar were recorded among the samples collected from Peshawar and Mardan.

The ANOVA results of lead level in KPK water are shown in Table 4. Lead was found significantly different in all districts (P=0.05) having the value of F=6.42 while the significant difference among different districts of KPK was 0.004.

Table 5 showed that the mean concentration of lead in the samples collected from Abbottabad were found significantly different to that of the concentration of lead collected from Peshawar while no significance difference was noted in the contents of lead collected from Mardan and DI Khan. The mean contents of lead in the samples collected from Peshawar showed significant difference from the contents of lead collected from Abbottabad, Mardan and DI Khan while there was no significant difference observed in the contents of lead among the mean lead contents in the samples collected from Abbottabad, Mardan and DI khan.

Table 1: Allowable Limits of Heavy Metals by various organization

Heavy Metals	Pak-EPA Limits (mg/L)	Canadian Limits (mg/L)	US Limits (mg/L)	WHO Limits (mg/L)
Ar	0.01	0.01	0.01	0.01
Pb	0.01	0.01	0.01	0.01
Cr	0.05	0.05	0.01	0.05
Cu	2	1	1.3	2
Zn	5	5	5	5

Table 2: ANOVA for Arsenic (µg/L) in drinking water collected from different districts of Khyber Pakhthoonkhwa (KPK)

		Arsenic KPK		
Source	Df	MS	F	P
Districts KPK	3	5.098E-05	15.3	0.0000
Error	196	3.322E-06	-	-
Total	199	-	-	-

df = degree of freedom, F = variance ratio

Table 3 : Arsenic concentration in drinking water collected from various sources of different districts of Khyber Pakhthoonkhwa (KPK)

	Arsenic (µg/L)					
	KPK				95% LC	
Districts KPK	No of sample	Minimum	Maximum	Mean ± SEM	Lower	Upper
Abbottabad	50	0.0000	2.980 E-03	5.311E-04^{c} ±8.914 E-05	3.520 E-04	7.103 E-04
Peshawar	50	0.0000	8.642 E-03	1.773E-03^{b} ±3.02.0 E-04	1.166 E-03	2.380 E-03
Mardan	50	0.0000	9.000 E-03	2.680E-03^{a} ±3.587 E-04	1.959 E-03	3.401 E-03
DI Khan	50	0.0000	7.932 E-03	6.741E-04^{c} ±1.950 E-04	2.823 E-04	1.065 E-03

Table 4: ANOVA for Lead (µg/L) in drinking water collected from selected districts of Khyber Pakhthoonkhwa (KPK)

		Lead KPK		
Source	Df	MS	F	P
Districts KPK	3	3.393E-06	6.42	0.0004
Error	196	5.289E-07	-	-
Total	199	-	-	-

df = degree of freedom, F = variance ratio

Table 5: Lead concentration in drinking water collected from various sources of different districts of Khyber Pakhthoonkhwa (KPK)

	Lead (µg/L)					
	KPK				95% LC	
Districts KPK	No of sample	Minimum	Maximum	Mean±SEM	Lower	Upper
Abbottabad	50	0.0000	1.890 E-03	9.380E-05^{b} ±5.110 E-05	-8.887 E-06	1.965 E-04
Peshawar	50	0.0000	7.542 E-03	5.447E-04^{a} ±1.992 E-04	1.443 E-04	9.451 E-04
Mardan	50	0.0000	0.0000	0.0000^{b} ±0.0000	0.0000	0.0000
DI Khan	50	0.0000	0.0000	0.0000^{b}±0.0000	0.0000	0.0000

Table 6: ANOVA for Chromium (µg/L) in drinking water collected from selected districts of Khyber Pakhthoonkhwa (KPK)

		Chromium KPK		
Source	Df	MS	F	P
Districts KPK	3	0.00314	3.35	0.0202
Error	196	0.00094	-	-
Total	199	-	-	-

df = degree of freedom, F = variance ratio

Table 7: Chromium concentration in drinking water collected from various sources of different districts of Khyber Pakhthoonkhwa (KPK)

	Chromium (µg/L)					
	Khyber Pakhthoonkhwa				95% LC	
Districts KPK	No of sample	Minimum	Maximum	Mean± SEM	Lower	Upper
Abbottabad	50	0.0000	0.4120	0.0172[a] ±8.646 E-03	-1.344 E-04	0.0346
Peshawar	50	0.0000	9.000 E-03	2.366E-03[b] ±4.101 E-04	1.541 E-03	3.190 E-03
Mardan	50	0.0000	9.000 E-03	1.062E-03[b]±3.198 E-04	4.192 E-04	1.705 E-03
DI Khan	50	0.0000	8.000 E-03	9.000E-04[b]±2.788 E-04	3.396 E-04	1.460 E-03

Table 8: ANOVA for Copper (µg/L) in drinking water collected from selected districts of Khyber Pakhthoonkhwa (KPK)

		Copper KPK		
Source	Df	MS	F	P
Districts KPK	3	0.05862	3.42	0.0175
Error	196	0.01695	-	-
Total	199	-	-	-

df = degree of freedom, F = variance ratio

The ANOVA for mean contents of chromium can be seen from Table 6 which revealed that all the samples collected from different districts of KPK showed significant difference 0.0202. The mean contents of chromium in the samples collected from different districts of KPK indicated significant difference ($P \leq 0.05$) having F value 3.35.

Table 7 data indicated that significant difference was observed in the mean concentration of chromium in the samples collected from district Abbottabad from all the samples of the other three districts of KPK i.e. Abbottabad, Mardan and DI khan. The mean value of chromium in samples collected from district Peshawar showed significant difference from the samples collected from district Abbottabad while no significant difference was noted in the samples collected from district Peshawar compare to that of chromium content in the samples of Mardan and DI khan. The samples collected from district Mardan also showed significant difference from the mean concentration of chromium contents in the samples collected from district Abbottabad while no significant difference was observed in the samples collected from the districts Peshawar and DI Khan. The mean chromium contents in the samples collected from district DI khan have significant difference from the samples of Abbottabad while no significant variation was observed in the samples of Peshawar and Mardan.

The ANOVA of Table 8 shows a significant difference (0.0175) for Copper contents among different districts of KPK. Copper was found significantly different in all districts ($P \leq 0.05$) having the value of F=3.42.

Table 9 revealed that the values of Cu in the samples of Abbottabad was significantly different from the samples collected from districts Mardan and DI Khan, while no significance difference in the mean concentration of copper was observed between Abbottabad and Peshawar. Significant difference was observed in the mean concentration of Cu in the samples collected from district Peshawar from that of the samples collected from districts Mardan and DI Khan and no significant

Table 9: Copper concentration in drinking water collected from various sources of different districts of Khyber Pakhthoonkhwa (KPK)

	Copper (µg/L)					
	Khyber Pakhtunkhawa				95% LC	
Districts KPK	No of sample	Minimum	Maximum	Mean± SEM	Lower	Upper
Abbottabad	50	0.0000	0.0000	0.0000^{b} ±0.0000	0.0000	0.0000
Peshawar	50	0.0000	0.0000	0.0000^{b} ±0.0000	0.0000	0.0000
Mardan	50	0.0000	0.7430	0.0415^{ab}±0.0201	9.791 E-04	0.0819
DI Khan	50	0.0000	1.0320	0.0701^{a} ±0.0308	8.096 E-03	0.1320

Table 10: ANOVA for Zinc (µg/L) in drinking water collected from selected districts of Khyber Pakhthoonkhwa (KPK)

		Zinc KPK		
Source	Df	MS	F	P
Districts KPK	3	697.250	13.7	0.0000
Error	196	51.030	-	-
Total	199	-	-	-

df = degree of freedom, F = variance ratio

Table 11: Zinc concentration in drinking water collected from various sources of different districts of Khyber Pakhthoonkhwa (KPK).

	Zinc (µg/L)					
	Khyber Pakhtunkhawa				95% LC	
Districts KPK	No of sample	Minimum	Maximum	Mean± SEM	Lower	Upper
Abbottabad	50	0.0000	35.000	10.849^{a} ±1.4422	7.9506	13.747
Peshawar	50	0.0000	32.000	5.7056^{b}±0.9960	3.7041	7.7071
Mardan	50	0.0000	17.000	2.8400^{bc} ±0.6709	1.4918	4.1882
DI Khan	50	0.0000	21.000	3.0200^{c} ±0.7486	1.5156	4.5244

Table 12: ANOVA for Arsenic (µg/L) in drinking water collected from selected districts of Punjab

		Arsenic Punjab		
Source	Df	MS	F	P
Districts Punjab	3	0.44665	0.79	0.5022
Error	196	0.56722	-	-
Total	199	-	-	-

df = degree of freedom, F = variance ratio

difference was recorded in the mean concentration of Cu in the samples collected from district Peshawar and district Abbottabad. The mean contents of Cu in the samples collected from district Mardan showed significant difference from the samples of districts Abbottabad, Peshawar and DI khan. The samples of district DI khan also showed significant difference from the samples collected from all the other three district of KPK (Abbottabad, Peshawar and Mardan).

The ANOVA of Zinc for all the districts of KPK can be observed from Table 10 which showed that significant difference was present in the samples of all the districts of KPK (0.000). The mean contents of Zinc in the samples collected from different districts of KPK indicated significant difference ($P \leq 0.05$) with F-value 13.7.

It is evident from Table 11 that the mean amount of Zn in the samples collected from district Abbottabad exhibited significant difference from the samples of Peshawar, Mardan and DI Khan. The mean concentration of Zn in the samples of Peshawar showed significant difference from the samples collected from districts Abbottabad, Mardan and DI Khan. The mean Zinc contents from district Mardan was significantly different from the contents of Zinc present in the samples of district DI khan, Peshawar and Abbottabad. The samples collected from district DI khan showed significant difference from that of the samples of Abbottabad, Mardan and Peshawar.

The ANOVA of Table 12 showed a significant difference (0.5022) for Arsenic among different districts of Punjab. Arsenic was found significantly different in all districts ($P \leq 0.05$) having the value of F=0.79.

Table 13: Arsenic concentration in drinking water collected from various sources of different districts of Punjab.

	Arsenic (µg/L)					
	Punjab				95% LC	
Districts Punjab	No of sample	Minimum	Maximum	Mean± SEM	Lower	Upper
Lahore	50	3.477 E-04	10.605	0.2147[a] ±0.2121	-0.2115	0.6408
Bahawalpur	50	0.0110	0.1084	0.0551[a]±3.814 E-03	0.0474	0.0628
Faisalabad	50	1.000 E-03	6.376 E-03	2.895E-03[a] ±2.021 E-04	2.489 E-03	3.301 E-03
Gujranwalla	50	1.020 E-03	1.0062	0.0338[a] ±0.0199	-6.202 E-03	0.0737

Table 14: ANOVA for Lead (µg/L) in drinking water collected from selected districts of Punjab

		Lead Punjab		
Source	Df	MS	F	P
Districts Punjab	3	2.872 E-05	2.29	0.0792
Error	196	1.251 E-05	-	-
Total	199	-	-	-

df = degree of freedom, F = variance ratio

Table 15: Lead concentration in drinking water collected from various sources of different districts of Punjab.

	Lead (µg/L)					
	Punjab				95% LC	
Districts Punjab	No of sample	Minimum	Maximum	Mean± SEM	Lower	Upper
Lahore	50	0.0000	9.000 E-03	2.062E-03[b] ±4.071 E-04	1.243 E-03	2.880 E-03
Bahawalpur	50	0.0000	0.0220	3.600E-03[a] ±6.851 E-04	2.223 E-03	4.977 E-03
Faisalabad	50	0.0000	8.000 E-03	1.956E-03 [b] ±3.578 E-04	1.236 E-03	2.675 E-03
Gujranwala	50	0.0000	0.0140	2.740E-03[ab] ±4.881 E-04	1.759 E-03	3.721 E-03

Table 13 revealed that mean concentration of Ar in the samples collected from district Lahore was not significantly different from that of all other three districts i.e. Bahawalpur, Faisalabad and Gujranwala, furthermore also there is no significant difference between all the districts of Punjab.

The ANOVA for mean contents of Lead for all districts of Punjab can be seen from Table 14 which revealed that all the samples showed significant difference 0.0792. The mean contents of Lead in the samples collected from different districts of Punjab indicated significant difference ($P \leq 0.05$) having F-value 2.29.

The mean concentration of lead in the samples of district Lahore was significantly different from the samples collected from district Bahawalpur and Gujranwala while there is no significant difference between the samples of Lahore and Faisalabad (Table 15).

The mean content of Pb in the samples collected from district Bahawalpur was significantly different from district Lahore, Faisalabad and Gujranwala.

It is evident from Table 16 that the ANOVA for mean concentration of chromium for all districts of Punjab that all the samples showed significant difference 0.0000. The mean contents of chromium in the samples collected from different districts of Punjab indicated significant difference ($P \leq 0.05$) having F- value 15.00.

Table 16: ANOVA for Chromium (µg/L) in drinking water collected from different districts of Punjab

		Chromium Punjab		
Source	Df	MS	F	P
Districts Punjab	3	3.230 E-04	15.0	0.0000
Error	196	2.151 E-05	-	-
Total	199	-	-	-

df = degree of freedom, F = variance ratio

Table 17: Chromium concentration in drinking water collected from various sources of different districts of Punjab

	Chromium (µg/L)					
	Punjab				95% LC	
Districts Punjab	No of sample	Minimum	Maximum	Mean± SEM	Lower	Upper
Lahore	50	0.0000	8.000 E-03	2.080E-03^{b} ±3.102 E-04	1.456 E-03	2.703 E-03
Bahawalpur	50	0.0000	6.000 E-03	6.800E-04^{b} ±1.905 E-04	2.972 E-04	1.062 E-03
Faisalabad	50	0.0000	5.000 E-03	5.200E-04^{b} ±1.857 E-04	1.468 E-04	8.932 E-04
Gujranwala	50	0.0000	0.0370	5.980E-03^{a} ±1.246 E-03	3.475 E-03	8.485 E-03

Table 18: ANOVA for Copper (µg/L) in drinking water collected from selected districts of Punjab

		Copper Punjab		
Source	Df	MS	F	P
Districts Punjab	3	3.97646	2.51	0.0602
Error	196	1.58569	-	-
Total	199	-	-	-

df = degree of freedom, F = variance ratio

Table 19: Copper concentration in drinking water collected from various sources of different districts of Punjab

	Copper (µg/L)					
	Punjab				95% LC	
Districts Punjab	No of sample	Minimum	Maximum	Mean± SEM	Lower	Upper
Lahore	50	0.0000	2.5000	0.6548^{ab} ±0.1084	0.4369	0.8727
Bahawalpur	50	0.0000	3.0000	0.6112^{ab} ±0.1224	0.3652	0.8572
Faisalabad	50	0.0000	2.8500	0.3336^{b}±0.0908	0.1512	0.5160
Gujranwala	50	0.0000	11.000	1.0202^{a}±0.3031	0.4111	1.6293

The mean concentration of chromium in the samples of district Lahore shown in Table 17 was significantly different from the samples collected from district Gujranwala while there is no significant difference between the samples of Lahore, Bahawalpur and Faisalabad.

The mean value of Cr in the samples collected from district Bahawalpur and Faisalabad was significantly different from district Gujranwala and there is non-significant difference in the mean concentration of Cr in the samples of Bahawalpur with that of Lahore and Faisalabad. The samples collected from district Gujranwala showed the significant difference with all the other three districts of Punjab i.e. Lahore, Faisalabad and Bahawalpur.

The ANOVA for mean contents of Copper can be seen from Table 18 which revealed that all the samples collected from different districts of Punjab showed significant difference 0.0602. The mean contents of Copper in the samples collected from different districts of Punjab indicated significant difference ($P \leq 0.05$) having F value 2.51.

Table 19 data indicated that significant difference was observed in the mean concentration of copper in the samples collected from district Lahore from the samples collected from districts Faisalabad and Gujranwala and there is no significant difference between the samples of Lahore and Bahawalpur.

Table 20: ANOVA for Zinc (µg/L) in drinking water collected from selected districts of Punjab

		Zinc Punjab		
Source	Df	MS	F	P
Districts Punjab	3	607.129	9.08	0.0000
Error	196	66.885	-	-
Total	199	-	-	-

df = degree of freedom, F = variance ratio

Table 21: Zinc concentration in drinking water collected from various sources of different districts of Punjab

	Zinc (µg/L)					
	Punjab				95% LC	
Districts Punjab	No of sample	Minimum	Maximum	Mean± SEM	Lower	Upper
Lahore	50	0.0000	35.000	10.380[a]±1.4142	7.5381	13.222
Bahawalpur	50	0.0000	36.000	10.431 [a] ±1.3913	7.6352	13.227
Faisalabad	50	0.0000	21.000	4.7702[b] ±0.6600	3.4439	6.0965
Gujranwala	50	0.0000	28.000	4.0172 [b] ±0.9897	2.0283	6.0061

Table 22: ANOVA for Arsenic (µg/L) in drinking water collected from selected districts of Sind

		Arsenic Sind		
Source	Df	MS	F	P
Districts Sind	3	0.42227	182	0.0000
Error	196	0.00232	-	-
Total	199	-	-	-

df = degree of freedom, F = variance ratio

The mean value of copper in samples collected from district Faisalabad showed significant difference from the samples collected from district Lahore, Bahawalpur and Gujranwala. The samples collected from district Gujranwala also showed significant difference from the mean concentration of copper contents in the samples collected from district Lahore, Bahawalpur and Faisalabad.

The ANOVA of Zinc for all the districts of Punjab can be observed from Table 20 which showed that significant difference was present in the samples of all the districts of Punjab (0.000). The mean contents of Zinc in the samples collected from different districts of KPK indicated significant difference ($P \leq 0.05$) with F-value 9.08.

It is evident from Table 21 that the mean amount of Zn in the samples collected from district Lahore exhibited significant difference from the samples of Faisalabad and Gujranwala while no significant difference was found in the samples of Lahore and Bahawalpur. The mean concentration of Zn in the samples of Bahawalpur showed significant difference from the samples collected from districts Faisalabad, Gujranwala and Faisalabad. The mean Zinc contents from district Faisalabad was significantly different from the samples of districts Gujranwala, Faisalabad and Bahawalpur.

The ANOVA for mean contents of Arsenic for all the districts of Sind can be observed from Table 22 which showed that significant difference was present in the samples of all the districts of Sind (0.000). The mean contents of Arsenic in the samples collected from different districts of KPK indicated significant difference ($P \leq 0.05$) with F-value 182.

It is evident from Table 23 that the mean amount of Arsenic in the samples collected from district Hyderabad exhibited significant difference from the samples of Tandoallahyar while no significant difference was found in the samples of Karachi and Sukkar. The mean concentration of Arsenic in the samples of Hyderabad, Karachi and Sukkar showed no significant difference while the mean Arsenic contents from district Tandoallahyar was also significantly different from the samples of districts Hyderabad, Karachi and Sukkar.

It is evident from Table 24 that the ANOVA for the concentration of Lead contents among all the districts of Sind were significantly different (0.0000). All the districts of Sind showed significant difference for mean arsenic contents ($P \leq 0.05$) with F- value 14.3.

The mean concentration of Lead in the samples collected from Hyderabad were found significantly different to that of the concentration of Lead collected from district Tandoallahyar while no significance difference was noted in the samples of Karachi and Sukkar. The mean contents of lead in the samples collected from Karachi showed significant difference from the contents of Lead collected from district Tandoallahyar

Table 23: Arsenic concentration in drinking water collected from various sources of selected districts of Sind

	Arsenic (µg/L)					
	Sind				95% LC	
Districts Sind	No of sample	Minimum	Maximum	Mean± SEM	Lower	Upper
Hyderabad	50	0.0000	0.1810	0.0155[b] ±5.000 E-03	5.500 E-03	0.0256
Karachi	50	2.092 E-04	6.981 E-03	1.583E-03[b]±1.804 E-04	1.221 E-03	1.946 E-03
Sukkar	50	0.0000	9.000 E-03	1.680E-03[b] ±4.337 E-04	8.084 E-04	2.552 E-03
Tandoallahyar	50	0.0500	0.4500	0.1896[a]±0.0127	0.1641	0.2151

Table 24: ANOVA for Lead (µg/L) in drinking water collected from selected districts of Sind

Lead Sind				
Source	Df	MS	F	P
Districts Sind	3	0.03348	14.3	0.0000
Error	195	0.00234	-	-
Total	198	-	-	-

df = degree of freedom, F = variance ratio

Table 25: Lead concentration in drinking water collected from various sources of selected districts of Sind

	Lead (µg/L)					
	Sind				95% LC	
Districts Sind	No of sample	Minimum	Maximum	Mean± SEM	Lower	Upper
Hyderabad	50	0.0000	7.321E-03	1.065E-03[b]±2.803 E-04	5.025 E-04	1.629 E-03
Karachi	50	0.0000	5.430E-03	5.914E-04[b] ±1.707 E-04	2.481 E-04	9.346 E-04
Sukkar	50	0.0000	0.0000	0.0000[b] ±0.0000	0.0000	0.0000
Tandoallahyar	50	0.0000	0.2500	0.0523[a]±0.0136	0.0249	0.0798

Table 26: ANOVA for Chromium (µg/L) in drinking water collected from selected districts of Sind

		Chromium Sind		
Source	Df	MS	F	P
Districts Sind	3	0.00364	22.6	0.0000
Error	196	0.00016	-	-
Total	199	-	-	-

df = degree of freedom, F = variance ratio

while there was no significant difference observed in the samples collected from Hyderabad and Sukkar. The mean contents of Lead in the samples collected from district Tandoallahyar was significantly different from all other three districts of Sind i.e. Karachi, Hyderabad and Sukkar.

The ANOVA for mean contents of chromium can be seen from Table 26 which revealed that all the samples collected from different districts of Sind showed significant difference 0.0000. The mean contents of chromium in the samples collected from different districts of Sind indicated significant difference ($P \leq 0.05$) having F- value 22.6.

Table 27 data indicated that significant difference was observed in the mean concentration of chromium in the samples collected from district Hyderabad from the samples of districts Karachi, Sukkar and Tandoallahyar. The mean value of chromium in samples collected from district Karachi showed significant difference from the samples collected from district Hyderabad, Sukkar and Tandoallahyar The samples collected from district Sukkar also showed significant difference from the mean concentration of chromium contents in the samples collected from districts Hyderabad, Karachi and Tandoallahyar while The mean

Table 27: Chromium concentration in drinking water collected from various sources of selected districts of Sind

	Chromium (µg/L)					
	Sind				95% LC	
Districts Sind	No of sample	Minimum	Maximum	Mean ± SEM	Lower	Upper
Hyderabad	50	0.0000	0.1140	0.0187[a]±3.372 E-03	0.0120	0.0255
Karachi	50	0.0000	0.0280	7.639E-03[b]±1.188 E-03	5.251 E-03	0.0100
Sukkar	50	0.0000	9.000E-03	1.402E-03[c] ±3.389 E-04	7.211 E-04	2.083 E-03
Tandoallahyar	50	0.0000	0.0000	0.0000[c] ±0.0000	0.0000	0.0000

Table 28: ANOVA for Copper (µg/L) in drinking water collected from selected districts of Sind

	Copper(Cu) Sind			
Source	Df	MS	F	P
Districts Sind	3	0.34020	5.18	0.0018
Error	195	0.06571	-	-
Total	198	-	-	-

df = degree of freedom, F = variance ratio

Table 29: Copper (Cu) concentration in drinking water collected from various sources of selected districts of Sind

	Copper (Cu) (µg/L)					
	Sind				95% LC	
Districts Sind	No of sample	Minimum	Maximum	Mean± SEM	Lower	Upper
Hyderabad	50	0.0000	0.0000	0.0000[b]±0.0000	0.0000	0.0000
Karachi	50	0.0000	2.6300	0.1888[a]±0.0636	0.0609	0.3167
Sukkar	50	0.0000	0.9720	0.0770[b]±0.0307	0.0153	0.1388
Tandoallahyar	50	0.0000	1.0000	0.0291[b]±0.0200	-0.0112	0.0694

Table 30: ANOVA for Zinc (µg/L) in drinking water collected from selected districts of Sind.

	Zinc (Zn) Sind			
Source	Df	MS	F	P
Districts Sind	3	692.425	14.90	0.0000
Error	195	46.559	-	-
Total	198	-	-	-

df = degree of freedom, F = variance ratio

chromium contents in the samples collected from district Sukkar and Tandoallahyar showed no significant difference.

The ANOVA for mean contents of Copper can be seen from Table 28 which revealed that all the samples collected from different districts of Sind showed significant difference 0.0018. The mean contents of Copper in the samples collected from different districts of Pakistan indicated significant difference ($P \leq 0.05$) having F-value 5.18.

Table 29 data indicated that significant difference was observed in the mean concentration of copper in the samples collected from district Hyderabad from the samples of district Karachi and there is no significant difference between the samples of Sukkar and Tandoallahyar. The mean amount of Copper in the samples of Karachi showed significant difference with all the other three districts of Sind i.e. Hyderabad, Sukkar and Tandoallahyar. The samples of Sukkar also showed significant difference with the samples collected from Karachi while no significant difference was observed in the mean concentration of Copper between the districts of Hyderabad and Tandoallahyar

Results tabulated in Table 30 showed that the ANOVA of mean concentration of Zinc for all the districts of Sind was significantly different (0.0000). The mean contents of Zinc in the samples collected from different districts of KPK indicated significant difference ($P \leq 0.05$) with F-value 14.90.

Table 31: Zinc (Zn) concentration in drinking water collected from various sources of selected districts of Sind

	Zinc (Zn) (µg/L)					
	Sind				95% LC	
Districts Sind	No of sample	Minimum	Maximum	Mean± SEM	Lower	Upper
Hyderabad	50	0.0000	35.000	8.4835^{b}±1.2323	6.0070	10.960
Karachi	50	0.0000	31.000	7.0642^{a}±1.1020	4.8486	9.2799
Sukkar	50	0.0000	29.000	5.8249^{b}±1.0106	3.7941	7.8558
Tandoallahyar	50	0.0000	0.0000	0.0000±0.0000	0.0000	0.0000

Table 32: ANOVA for Arsenic (µg/L) in drinking water collected from selected districts of Balochistan

	Arsenic Balochistan			
Source	Df	MS	F	P
Districts Baluchistan	3	0.00123	9.20	0.0000
Error	196	0.00013	-	-
Total	199	-	-	-

df = degree of freedom, F = variance ratio

Table 33: Arsenic concentration in drinking water collected from various sources of selected districts of Balochistan

	Arsenic (µg/L)					
	Balochistan				95% LC	
Districts Balochistan	No of sample	Minimum	Maximum	Mean± SEM	Lower	Upper
Quetta	50	1.306 E-04	9.307 E-03	9.224E-04^{b} ±1.857 E-04	5.493 E-04	1.295 E-03
Jaffarabad	50	0.0000	0.0537	0.0111^{a}±1.386 E-03	8.340 E-03	0.0139
Turbat	50	0.0000	0.0310	8.702E-03^{a} ±1.121 E-03	6.447 E-03	0.0110
Zhob	50	0.0000	0.0996	0.0116^{a}±2.728 E-03	6.153 E-03	0.0171

It is evident from Table 31 that the mean amount of Zn in the samples collected from district Hyderabad exhibited significant difference from the samples of Karachi while no significant difference was found in the samples of Sukkar and Tandoallahyar. The mean concentration of Zn in the samples of Karachi showed significant difference from the samples collected from districts Hyderabad, Sukkar and Tandoallahyar. The mean Zinc contents from district Sukkar also showed significant difference from that of Karachi while no significant difference was seen between the other districts Hyderabad and Sukkar.

The ANOVA for mean contents of Arsenic for all the districts of Balochistan can be observed from Table 32 which indicated that significant difference was present in the samples of all the districts of Balochistan (0.000). The mean contents of Arsenic in the samples collected from different districts of Balochistan indicated significant difference ($P \leq 0.05$) with F-value 9.20.

It is evident from Table 33 that the mean amount of Arsenic in the samples collected from district Quetta exhibited significant difference from the samples of Jaffarabad while no significant difference was found in the samples collected from Jaffarabad, Turbat and Zhob.

The ANOVA for mean contents of Lead for all districts of Balochistan can be seen from Table 34 which revealed that all the samples showed significant difference 0.0002. The mean contents of Lead in the samples collected from different districts of Balochistan indicated significant difference ($P \leq 0.05$) having F-value 6.89.

The mean concentration of Lead in the samples of district Quetta was significantly different from the samples collected from district Turbat and Zhob while there is no significant difference between the samples of Quetta and Jaffarabad. The mean content of Pb in the samples collected from district Jaffarabad was also significantly different from district Turbat and Zhob. The mean Lead concentration in the samples collected from districts Turbat and Zhob did not show any significant difference.

Table 34: ANOVA for Lead (µg/L) in drinking water collected from selected districts of Balochistan

		Lead Balochistan		
Source	Df	MS	F	P
Districts Balochistan	3	5.657 E-06	6.89	0.0002
Error	195	8.211 E-07	-	-
Total	198	-	-	-

df = degree of freedom, F = variance ratio

Table 35: Lead concentration in drinking water collected from various sources of selected districts of Balochistan

	Lead (µg/L)					
	Balochistan				95% LC	
Districts Balochistan	No of sample	Minimum	Maximum	Mean± SEM	Lower	Upper
Quetta	50	0.0000	6.510 E-03	5.571E-04[a] ±1.901 E-04	1.751 E-04	9.391 E-04
Jaffarabad	50	0.0000	4.370 E-03	6.087E-04[a] ±1.709 E-04	2.652 E-04	9.522 E-04
Turbat	50	0.0000	0.0000	0.0000[b] ±0.0000	0.0000	0.0000
Zhob	50	0.0000	0.0000	0.0000[b]±0.0000	0.0000	0.0000

Table 36: ANOVA for Chromium (µg/L) in drinking water collected from selected districts of Balochistan

		Chromium Balochistan		
Source	Df	MS	F	P
Districts Balochistan	3	1.239 E-04	2.16	0.0940
Error	194	5.733 E-05	-	-
Total	197	-	-	-

df = degree of freedom, F = variance ratio

Table 37: Chromium concentration in drinking water collected from various sources of selected districts of Balochistan.

	Chromium (µg/L)					
	Baluchistan				95% LC	
Districts Balochistan	No of sample	Minimum	Maximum	Mean± SEM	Lower	Upper
Quetta	50	0.0000	0.0000	0.0000[b] ±0.0000	0.0000	0.0000
Jaffarabad	50	0.0000	0.0843	2.851E-03[ab]±1.713 E-03	-5.902 E-04	6.293 E-03
Turbat	50	0.0000	0.0215	3.596E-03[a]±7.191 E-04	2.150 E-03	5.041 E-03
Zhob	50	0.0000	0.0320	2.708E-03[ab]±1.087 E-03	5.198 E-04	4.897 E-03

Table 36 shows the ANOVA for mean contents of chromium which revealed that all the samples collected from different districts of Balochistan showed significant difference 0.0940. The mean contents of chromium in the samples collected from different districts of Balochistan indicated significant difference ($P \leq 0.05$) having F-value 2.16.

Results tabulated in Table 37 indicated that significant difference was observed in the mean concentration of chromium in the samples collected from district Quetta from the samples of districts Jaffarabad, Turbat and Zhob. The mean value of chromium in samples collected from district Jaffarabad showed significant difference from the samples collected from district Quetta, Turbat and Zhob. The samples collected from district Turbat also showed significant difference of the mean concentration of chromium contents in the samples collected from districts Zhob, Quetta and Jaffarabad.

The ANOVA of Table 38 did not show any significant difference (0.0000) for Copper contents among different districts of Balochistan. Copper was found significantly different in all districts (P=0.05) having

Table 38: ANOVA for Copper (µg/L) in drinking water collected from selected districts of Balochistan

Copper (Cu) Balochistan				
Source	Df	MS	F	P
Districts Balochistan	3	0.0000	M	M
Error	194	0.0000	-	-
Total	197	-	-	-

df = degree of freedom, F = variance ratio

Table 39: Copper (Cu) concentration in drinking water collected from various sources of selected districts of Balochistan.

	Copper (Cu) (µg/L)					
	Baluchistan				95% LC	
Districts Balochistan	No of Sample	Minimum	Maximum	Mean ± SEM	Lower	Upper
Quetta	50	0.0000	0.0000	0.0000±0.0000	0.0000	0.0000
Jaffarabad	50	0.0000	0.0000	0.0000±0.0000	0.0000	0.0000
Turbat	50	0.0000	0.0000	0.0000±0.0000	0.0000	0.0000
Zhob	50	0.0000	0.0000	0.0000±0.0000	0.0000	0.0000

Table 40: ANOVA for Zinc (µg/L) in drinking water collected from selected districts of Balochistan

Zinc (Zn) Balochistan				
Source	Df	MS	F	P
Districts Baluchistan	3	948.735	21.2	0.0000
Error	194	44.697	-	-
Total	197	-	-	-

df = degree of freedom, F = variance ratio

Table 41: Zinc (Zn) concentration in drinking water collected from various sources of selected districts of Balochistan

	Zinc (Zn) (µg/L)					
	Balochistan				95% LC	
Districts Balochistan	No of sample	Minimum	Maximum	Mean± SEM	Lower	Upper
Quetta	50	0.0000	23.410	3.4373^{b}±0.8116	1.8062	5.0684
Jaffarabad	50	0.0000	36.240	11.156^{a}±1.4519	8.2371	14.076
Turbat	50	0.0000	12.650	1.9474^{b}±0.5476	0.8464	3.0484
Zhob	50	0.0000	31.000	2.0400^{b}±0.7543	0.5242	3.5558

the value of F=M. Table 39 revealed that the values of Cu in the samples collected from all the districts of Balochistan was not significantly different from each other i.e. Quetta, Jaffarabad, Turbat and Zhob.

The ANOVA of Zinc for all the districts of Balochistan can be observed from Table No 40 which showed that significant difference was present in the samples of all the districts of Balochistan (0.000). The mean contents of Zinc in the samples collected from different districts of Balochistan indicated significant difference ($P \leq 0.05$) with F-value 21.2.

It is evident from Table 41 that the mean amount of Zn in the samples collected from district Quetta exhibited significant difference from the samples of Jaffarabad while does not showed any significant difference with that of the samples collected from district Turbat. The mean concentration of Zn in the samples of Jaffarabad showed significant difference from the samples collected from districts Quetta, Turbat and Zhob. The mean Zinc contents from districts Turbat and Zhob also showed significant difference from the samples of district Jaffarabad while no significant difference was observed from the samples collected from district Quetta.

DISCUSSION

Heavy Metals Health Risk Assessment: Arsenic (Ar) is one of the hazardous metalloids present in the drinking water, resulting from both anthropogenic and geogenic sources [19] It has many chemical forms that differ not only with regards to physical, chemical and biological properties but also have different toxicities [20]. Both the

organic and inorganic Ar species are toxic in nature but the inorganic species are considered more toxic as compared to organic species [21]. Arsenic not only contaminates surface and groundwater but also enters into food chains like vegetables and food staff [22]. The ingestion of Ar contaminated drinking water can cause serious health problems including cancer, melanosis, hyperkeratosis, restrictive lung disease, gangrene, hypertension and peripheral vascular disease [23 and 24] skin lesion [25 and 26]. As well as its carcinogenic effect on lungs and skin [27].

Lead compounds have been with us for many decades. The massive application of lead in household utensils and water pipelines dates back to the Roman Empire. Industrialization through industrial activities and vehicle emissions, especially in big urban cities where there are large numbers of vehicles on the road, compound the problem of lead pollution on the global scale. Lead has been recognized as one of 'the big three' of heavy metals (together with cadmium and mercury) that have high toxicity and its accumulation leads to health issues in living tissues [28] reported that lead poisoning leads to a condition known as plumbism, colica, Pictonum, saturnism which is a medical condition caused by exposure to increased levels of lead in the body. Lead is regarded as toxic pollutant due to its severe or hazards potential to the environment and organisms.

Chromium is used in the leather tanning industry, the manufacturing of catalyst, pigment and paints, fungicides, the ceramics and glass industries. Chromium within the recommended limit in drinking water is essential in human nutrition to maintain the normal glucose metabolism. However, if higher than the recommended level, it causes nephritis and glycosuria [29, 30].

CONCLUSIONS

In the present study elemental analysis of various water samples taken from all over the Pakistan was carried out. Five heavy metals *viz.* Ar, Pb, Cr, Cu and Zn were analyzed. Most of the samples were found within the permissible limits set by WHO, Pk-EPA and US-EPA while some parameters were above the permissible limits. The water can be used for drinking purposes unless it is passed through special water treatment. People may suffer through disease on drinking water with higher concentration of heavy metals. They may have physiological effects on kidney, digestive system, circulatory system, nervous system etc. various other organs and various systems of the body.

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